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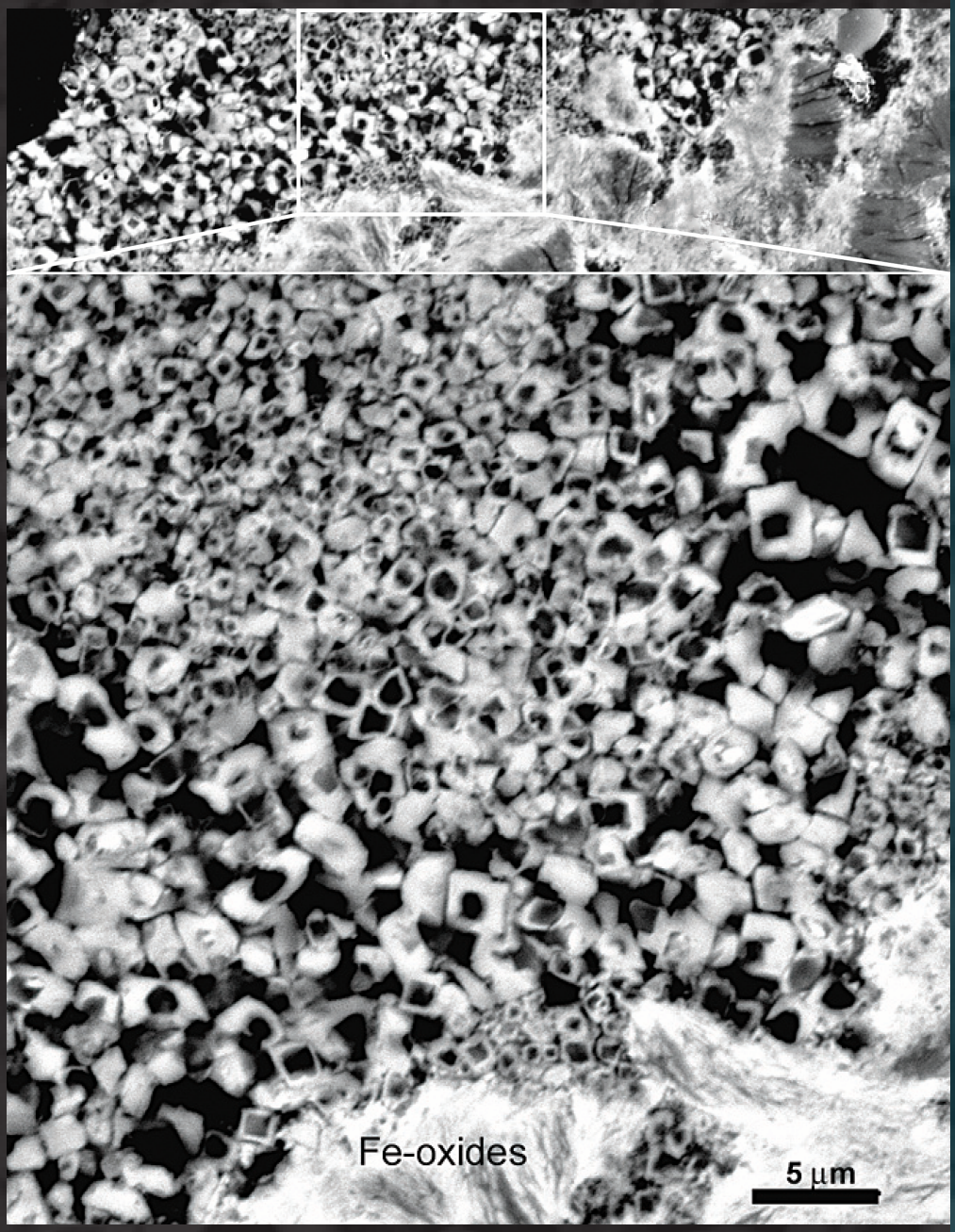
Methods for Synthesis of Some Jarosites



SEM image of naturally occurring hollow jarosite magnified approximately 3,500 times.

Techniques and Methods 5-D1

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By Rhonda L. Driscoll and Reinhard W. Leinz

Book 5—Laboratory Analysis
Section D—Geologic Analysis
Chapter 1

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Abstract

Experimental procedures described in this report summarize attempts to synthesize potassium-, hydronium-, sodium-, and mixed-composition (hydronium-bearing) jarosites ($KFe_3(SO_4)_2(OH)_6$). For some experiments we duplicated or modified published synthesis methods; for others we designed new experiments. Initially, we were unable to predict ideal synthesis time and temperature conditions, product yields, or product composition. However, after experimentation, some acceptable combinations of chemical and physical factors were found to routinely synthesize chemically different jarosites. The mineralogical composition of synthetic substances was identified using a Shimadzu XRD 6000 instrument, Jade reduction software–Version 5, and ICDD Powder Diffraction Files–Release 2002. The synthetic products were used as part of a characterization study of some natural and synthetic jarosites.

Methods

Experimental Methods for Synthesis of End-Member K-Jarosite

The method of Baron and Palmer (1996) was used first to synthesize end-member K-jarosite; 17.2 g of ferric sulfate hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$) and 5.6 g of potassium hydroxide (KOH) were dissolved in 100 mL 18MΩ water[1]. The solution was prepared in a covered glass beaker and placed on a 95°C stirring hot plate. A moderate boil was maintained for 4 hours; the solution was then removed from the stirring plate and the precipitate was allowed to settle. Once settling occurred, the liquid phase was carefully decanted and the precipitate was rinsed twice with deionized water. The rinsate was discarded and the solid remains were placed in a 110°C drying oven for 24 hours. After drying, the substance was collected and weighed; about 9 g of jarosite was produced (table 1, Sample 1). The product was analyzed using inductively coupled plasma–mass spectrometry (ICP-MS). ICP-MS analysis confirmed the presence of end-member K-jarosite (Desborough and others, 2004).

The synthesis was repeated using half as much KOH (2.80 g). Amounts of ferric sulfate hydrate and 18MΩ water were not changed. Heating method, temperature, time, and drying conditions were the same as those preceding. The second preparation yielded 7.7 g of a mixed-composition jarosite—$K_{0.85}H_3O_{0.15}Fe_3(SO_4)_2 \cdot (OH)_6$—based on ICP-MS analysis of potassium (table 1, Sample 2).

Four additional preparations, using 17.2 g of ferric sulfate hydrate and 3.1, 2.6, 2.2, and 1.4 g of KOH, respectively, dissolved in 100 mL 18MΩ water, were prepared in the same way (table 1, Samples 3, 4, 5). Hydronium-bearing jarosites of different composition were produced.

The next synthesis required 17.2 g of ferric sulfate to be dissolved in 100 mL 18MΩ water. KOH was excluded. After heating and drying, the only mineral produced was a minute amount of schwertmannite ($Fe^{3+}_{16}O_{16}(OH)_{12}(SO_4)_2$), which was identified using X-ray diffraction (XRD).

The final preparation based on the Baron and Palmer (1996) method required dissolution of 6.56 g $Fe_2(SO_4)_3 \cdot nH_2O$ in 100 mL 18MΩ water. No other reagents were used. As in previous experiments, the solution was heated at 95°C for 4 hours on a stirring hot plate. It was then allowed to cool for 2 hours, during which time it remained an amber liquid without any visible precipitate. The pH of this and the previous preparation liquid phase was less than 1. The pH of solution is significant because jarosite formation favors a pH range of 1.3 to 3.5 (G.A. Desborough, oral commun., 2004).

Experimental Method for Synthesis of Mixed-Composition Jarosite

In this series of syntheses, preparations one and two made use of a goethite slurry. The slurry was made beforehand by (1) dissolving 25.0 g ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 412.5 mL deionized water, (2) dissolving 28.0 g potassium hydroxide (KOH) in 200 mL deionized water to produce a 2.5N solution of KOH, and (3) adding 100 mL of the 2.5N KOH solution to the entire ferric nitrate solution and swirling to mix in a heat-resistant Nalgene bottle. The mixture was then loosely capped

[1] Three grades of water are used in the laboratory: distilled water, deionized water, and 18MΩ, or ultra-pure water. Distilled water is water that has been heated and converted to steam and then cooled and condensed. The process concentrates dissolved solids that resist vaporization. Deionized water is water that is passed through a resin column to remove electrically charged, or ionized, dissolved particles. The ionized particles collect on the resin column. Most resin compositions are proprietary. 18MΩ, or ultra-pure water, is water that has been distilled, deionized, *and* passed through an activated carbon filtration system to remove trace bacteria and other impurities. 18MΩ water is a poor electricity conductor.

and placed in a drying oven, preheated to 60°C, for 24 hours. After the bottle was removed from the drying oven, the mixture was given time to cool at room temperature and to separate into distinct liquid and solid phases. After the liquid phase was decanted, the solid remains were washed with 500 mL deionized water, allowed to settle and separate, decanted, and rewashed overnight with 250 mL deionized water. An aliquot of the initial decant was reserved for pH measurement. The wash process was repeated for 6 consecutive days or until the pH of the decant solution measured 8.1. The final product had a watery consistency and was identified as goethite using XRD.

For the first synthesis in this series, 5.0 g of goethite slurry was mixed with 100 mL of 0.5N sulfuric acid (H_2SO_4). The mixture was heated in a glass beaker on a 95°C stirring plate for 3 hours. After the beaker was removed from the stirring plate, the liquid phase was decanted. The solid remains were placed in a 110°C drying oven for 18 hours. Prolonged drying produced a reddish-brown glutinous substance. Litmus paper indicated a highly acidic compound; XRD analysis identified a generic iron sulfate.

The next synthesis in this series required dissolution of 16.0 g $Fe_2(SO_4)_3 \cdot nH_2O$ in 100 mL 18MΩ water in a glass beaker; dissolution took about 3 minutes. Four grams of synthetic goethite slurry was then added, and the mixture was placed on a ≈75°C stirring plate. After 3 hours, the solution was transferred to a drying oven (preheated to 110°C) for 48 hours. The dried product, when removed from the oven, resembled brittle, beige "taffy." X-ray analysis indicated a generic ferric sulfate.

Experimental Method for Synthesis of Natrojarosite

The initial attempt to synthesize natrojarosite entailed dissolution of 17.2 g $Fe_2(SO_4)_3 \cdot nH_2O$ and 4.0 g NaOH in 100 mL 18MΩ water in a 250 mL glass beaker. The solution was brought to a slow boil on a stirring plate and left undisturbed for 4 hours. As in previous synthesis procedures, the solution was removed from the heat, decanted, rinsed with 100 mL deionized water, and dried overnight at 100°C. The dried product, verified by XRD as end-member natrojarosite, weighed 20.7 g.

The synthesis was repeated using one-quarter as much NaOH (1.0 g). In all other ways, the second sodium preparation duplicated the first. Not surprisingly, the second preparation yielded less than one-quarter the amount of product, or 2.3 g of natrojarosite.

Improved Experimental Method for Synthesis of Mixed-Composition Jarosite

For our next series of syntheses, we began with six 50 mL capped polypropylene tubes, each containing 2.8 g $Fe_2(SO_4)_3 \cdot nH_2O$ and 13 g 18MΩ water. The tubes were labeled I–VI. A specific weighed amount of 22.5 percent KOH solution was added to each tube:

Tube I	5.60 g KOH soln.	Tube IV	0.46 g KOH soln.
Tube II	2.80 g KOH soln.	Tube V	0.24 g KOH soln.
Tube III	1.40 g KOH soln.	Tube VI	0.12 g KOH soln.

After the KOH solution was added, all tubes were shaken vigorously by hand. The content of each tube was then transferred to a corresponding Teflon bomb. Each bomb was sealed in a steel cylinder and placed in a furnace for 5 hours at 140°C. After removal from the furnace and a brief cooling interval, the six bombs were unsealed. The liquid from each bomb was decanted, and the solid remains were scraped from the Teflon vessel. The scrapings were washed with deionized water onto a Whatman #42 ashless filter paper molded inside a vacuum funnel. The funnel itself was fixed firmly over a vacuum flask. In this way most of the residual fluid was removed from the solid product with the product itself accumulating on the filter paper. The filter paper was then transferred to a drying oven. After 1 hour in the oven (60°C), five of the six syntheses yielded fine powders. The composition of the powders, using both standard XRD identification and a computer-based cell-refinement routine, was verified as hydronium-bearing jarosite. Yields were proportionate to the amount of KOH present in each solution:

Tube II	1.84 g	Tube V	0.69 g
Tube III	1.32 g	Tube VI	0.53 g.
Tube IV	1.19 g		

Preparation I failed to produce jarosite.

To determine the roles of time and temperature in jarosite formation, we again dissolved varying amounts of 22.5 percent KOH reagent in a fixed ferric sulfate hydrate solution (2.58 g $Fe_2(SO_4)_3 \cdot nH_2O$ dissolved in 13 g 18MΩ water):

Tube I	1.870 g KOH soln.	Tube IV	0.240 g KOH soln.
Tube II	0.939 g KOH soln.	Tube V	0.120 g KOH soln.
Tube III	0.467 g KOH soln.		

Sealed inside their own Teflon vessel, each mixture was heated for 4 hours at 100°C—a reduction of time and temperature of 1 hour and 40°C, respectively. These deliberate changes in synthesis conditions did not affect product composition (hydronium-bearing jarosite was confirmed by X-ray analysis), but did affect product mass:

Tube I	0.98 g	Tube IV	0.45 g
Tube II	0.71 g	Tube V	0.30 g.
Tube III	0.59 g		

Because of the reduction of time and temperature of reaction, some of the reagent remained in solution, limiting the product mass. As the quantities of these syntheses were small, we did not use these materials for chemical studies.

Improved Experimental Method for Synthesis of End-Member Hydronium Jarosite

One of our earliest syntheses was intended to produce hydronium jarosite. By combining $Fe_2(SO_4)_3 \cdot nH_2O$ and water only, we hoped to synthesize a hydronium end-member. The experiment, conducted in a covered glass beaker on a hot plate, produced only a trace amount of schwertmannite. We reconsidered the synthesis and subsequently modified it by replacing the beaker and hot plate with a 200 mL Teflon bomb and furnace.

The first of the modified synthesis trials required dissolution of 20 g of ferric sulfate hydrate in a glass beaker containing 150 mL 18MΩ water. The ferric solution was poured into a large Teflon vessel, which was sealed inside a heavy steel canister. The Teflon bomb was heated for 5 hours in a 140°C furnace. After removal from the furnace, the bomb was allowed to cool at room temperature for 2 hours. The solid phase was then extracted from the bomb and dried for 1 hour in a 60°C oven. A scant 0.16 g of hydronium jarosite was recovered. A second, identical bomb synthesis yielded 1.02 g of hydronium jarosite. The significant difference in yields was attributed to an unreliable temperature control on the furnace used to heat the first solution. Because hydronium jarosite was unmistakably identified using XRD, we were able to "mass produce" this desirable end-member following our modified method. In all, we made 13.5 g of H_3O-jarosite with an average 0.83 g of product per synthesis.

Improved Method for Synthesis of End-Member K-Jarosite

Of the many Teflon bomb syntheses conducted, we recorded negligible fluid loss during heating. Whether initiating the synthesis with 15 mL or 150 mL of solution, we consistently decanted the same liquid volume after heating. The only exception to this trend occurred during production of K-jarosite.

The K-jarosite solution was prepared by dissolving 25.8 g $Fe_2(SO_4)_3 \cdot nH_2O$ in a 250 mL glass beaker containing 130 mL 18MΩ water. Next, 18.7 g of 45 percent KOH solution was added and mixed thoroughly by hand shaking. Additional 18MΩ water was added to bring the solution to 150 mL. Following transfer to a 200 mL Teflon bomb, the solution was placed in a furnace and heated for 5 hours at 140°C. After cooling at room temperature, the liquid phase was decanted into a graduated cylinder. For the first time, fluid loss was measurable. Approximately 50 mL had been lost or consumed during heating. The solid phase was also atypical. After drying overnight in a 60°C oven, the solid had separated into discrete yellow and red layers. The yield, too, was unexpected—an impressive 16.33 g (table 1, Sample 6).

The entire experiment was performed a second time with near-identical results—a 50 mL fluid loss after heating, color separation during prolonged low-temperature drying, and recovery of 16.29 g of product (table 1, Sample 7).

These two syntheses produced a near-end-member jarosite (97 mol. percent K) and a hydronium-bearing jarosite (86 mol. percent K), respectively.

Low-Temperature Jarosite Synthesis

To determine if end-members K-jarosite and hydronium-jarosite mix in a straight line at known quantity intervals, we conducted a final series of syntheses. All products from this series were systematically X-rayed and plotted.

The first synthesis called for 17.2 g $Fe_2(SO_4)_3 \cdot nH_2O$, 100 mL 18MΩ water, and 5.6 g KOH. The mixture was heated in a loosely covered glass beaker on a magnetic stirring hot plate. Hot plate temperature was set at 95°C. Heating time was 3 hours. After removal from the stirring hot plate, the beaker was placed inside a preheated drying oven for 12 hours. Drying temperature was 60°C.

The second and third synthesis attempts required 17.2 g ferric sulfate hydrate, 100 mL 18MΩ water, and 2.8 g KOH and 1.4 g KOH, respectively. Each solution was mixed in a glass beaker, heated on a 95°C stirring hot plate for 3 hours, and dried for 12 hours at a constant temperature of 60°C.

The dried product of the first synthesis appeared as a fluffy pale-orange solid topped by a fine white crust. The products of the second and third syntheses were brittle and dark orange in color. All products were identified by XRD as something other than jarosite.

The next low-temperature synthesis series was performed in a closed system. The first of the series combined 5.6 g KOH with 17.2 g ferric sulfate hydrate and 100 mL 18MΩ water. After stirring to dissolve and mix reagents, the solution was poured into a Teflon bomb and sealed inside a thick-walled steel canister. The canister was placed in a furnace preheated to 95°C. After heating for 3 hours, the canister was removed from the furnace and allowed to cool at room temperature for one-half hour. When the internal Teflon bomb was opened, its liquid content was poured through a Whatman #2 ashless filter paper. A fine-grained brick-red solid accumulated on the filter paper. The solid was rinsed with deionized water to remove residual acid. A yellow-orange solid was then scraped from the bottom and sidewalls of the Teflon vessel, washed onto another #2 ashless filter paper, and rinsed thoroughly with deionized water. The filter papers containing both the red and yellow-orange solids were placed on watch glasses and moved into a 60°C drying oven for 1 hour. Each dried solid phase weighed 3.5 g (table 1, Sample 8; table 2, products details).

The synthesis was repeated using decreasing amounts of KOH: 2.8 g, 1.4 g, 0.7 g, and 0.3 g (table 1, Samples 9, 10, 11, 12; table 2, products details). The amount of iron (III) sulfate and the volume of 18MΩ water were unchanged for each synthesis. Furnace and oven temperatures and heating and drying times were also constant.

Table 1. At-a-glance synthesis conditions for in-text numbered samples.

[Mol percent K determined by ICP-MS]

Sample number (beaker, stirring hot plate)	$(Fe_2(SO_4)_3 \bullet nH_2O)$ (g)	KOH (g)	18MΩ water (mL)	Heating time and temperature	Drying time and temperature	mol % K
1	17.2	5.6	100	95°C/4 hours	110°C/24 hours	1
2	17.2	3.1	100	95°C/4 hours	110°C/24 hours	0.88
3	17.2	2.8	100	95°C/4 hours	110°C/24 hours	0.85
4	17.2	2.6	100	95°C/4 hours	110°C/24 hours	0.86
5	17.2	1.4	100	95°C/4 hours	110°C/24 hours	0.76
Sample number (Teflon bomb, furnace)		**45% KOH soln. (g)**				
6	25.8	18.7	≈130	140°C/5 hours	60°C/18 hours	0.97
7	25.8	18.7	≈130	140°C/5 hours	60°C/24 hours	0.86
Sample number (Teflon bomb, furnace)		**KOH (g)**				
8	17.2	5.6	100	95°C/3 hours	60°C/1 hour	0.91
9	17.2	2.8	100	95°C/3 hours	60°C/1 hour	0.85
10	17.2	1.4	100	95°C/3 hours	60°C/1 hour	1.76
11	17.2	0.7	100	95°C/3 hours	60°C/1 hour	0.73
12	17.2	0.3	100	95°C/3 hours	60°C/1 hour	0.71

Table 2. Yield results for low-temperature jarosite syntheses using different amounts of KOH.

[The fine products accumulated on the filter paper during initial decant. The coarse products were scraped off the sidewalls and bottom of the Teflon vessel used in the preparation. Both products were washed thoroughly with deionized water prior to drying]

Amount of KOH[1]	Yield 1	Yield 2	Type jarosite
(8) 5.6 g	3.5 g fine brick-red solid	3.5 g coarse yellow-orange solid	Both mixed composition
(9) 2.8 g	1.5 g fine dark red	3.0 g coarse dark yellow	Both mixed composition
(10) 1.4 g	1.5 g fine dark yellow	2.5 g coarse light brown	Both mixed composition
(11) 0.7 g	2.0 g fine dark yellow		Single mixed composition
(12) 0.3 g	0.7 g fine light yellow		Single mixed composition

[1]Numbers in parentheses added to correspond to entries in table 1.

The entire synthesis was repeated a second time. Identical decreasing amounts of KOH were added to the same mixture of ferric sulfate hydrate (17.2 g) and 18MΩ water (100 mL). Each solution was heated for 3 hours at 95°C, cooled for one-half hour, decanted through a #2 ashless filter paper, and dried for 1 hour in a preheated 60°C drying oven. The results of the duplicate synthesis were somewhat different from those of the first closed system series: product weights and compositions were comparable, but the color banding and fine-coarse distinctions did not occur—all products were uniformly fine grained and light yellow in color.

We are unaware of any furnace or drying oven temperature fluctuations or any reagent contamination. Heating and drying intervals were precisely timed. All reagents were weighed on the same toploading digital balance. Balance accuracy was verified prior to use. All glassware was prewashed with a cleanroom general purpose detergent, and all possible sources of cross contamination were removed from the work space. How then could the product of each duplicate synthesis differ in *quality*? At present this question is under investigation.

The type of jarosite for all the duplicate series syntheses was determined to be hydronium-bearing-jarosite.

Conclusion

Only after months of experimentation were we able to synthesize four distinct species of jarosite in significant quantities—end-members K-jarosite, hydronium jarosite and sodium jarosite, and variable mixed-composition jarosite. In addition, we were able to demonstrate that jarosite forms under very specific chemical and physical conditions in the laboratory. Those conditions include ratios of iron, sulfur, sodium, and potassium to water; synthesis temperature and time; and especially acidity of the formation environment. An open system, such as that involving use of a glass beaker and magnetic stirring hot plate, permits fluid loss. Fluid loss, in turn, whether through evaporation or some other means, affects the pH of solution. Jarosite, we now know, forms in a narrow pH range. A closed system eliminates the probability of fluid loss. Jarosite synthesis requires a stable fluid volume at a controlled pH.

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